International Journal of Engineering Research (ISSN : 2319-6890)
Volume No.2, Issue No.2, pp : 58-61 01 April 2013

Reduction of Ice Consumption in Vinyl Sulphone Industry

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Abstract

Conventional Vinyl Sulphone manufacturing generates corrosive and acidic gases and liquid effluent, which is highly toxic with high BOD, COD and TDS values. Gaseous emissions can be effectively scrubbed. However, liquid effluent requires large quantity of lime to neutralise and it generates large quantity of gypsum containing organic impurities.The reduction or elimination of ice usage in dye industry is a key to reduce liquid effluent generated in the process. This paper describes the use of external cooling in the form of jacket or heat exchanger in the dumping step of the manufacturing process whereby the direct addition of ice in the dumping vessel is eliminated. Only the water needed for decomposing excess of chlorosulphonic acid needs to be added. The reduced amount of water in this step would result in less effluent generation. Moreover, the dilution of spent acid is reduced which can find some use at other places. Additional advantage is that the HCl recovery is easier from concentrated spent acid. This paper also shows that the yield of the desired product ASC (Acetyl Sulphonyl Chloride) obtained experimentally is higher than that found in the conventional process.

Key words – Acetyl Sulphonyl Chloride, Chlorosulphonation, Chlorosulphonic acid

I. INTRODUCTION

The Dyes & Dye intermediate sector is one of the core chemical industries in India. It is also the second highest export segment in chemical industry. The vinyl sulphones are extensively used as the diazo reactive components for the manufacture of reactive dyes. The production of vinyl sulphone has shown a quantum jump in India in last two decades and it has the highest volume of export among the dye intermediates. However, the conventional method of manufacturing vinyl sulphone results in generation of large amounts of liquid effluent having higher BOD, COD and TDS values. This is mainly due to the over usage of ice for maintenance of low temperatures. Around 30000 Kg of ice is used for every single batch. This excessive reliance on ice has also resulted in problems like dilution of spent acid, difficulty in the precipitation of sulphanillic acid which is a byproduct of the process.

So, laying the focus on reduction or elimination of ice consumption in the vinyl sulphone industry is vital. Alternate methods for maintaining low temperature in the dumping vessel have been explored in the literature and various options have been found. Use of slurry ice , use of energy balls filled with phase changing materials, alternative routes for manufacturing vinyl sulphone which eliminates the dumping step, indirect cooling and use of alternative raw materials which use tertrachloro-ethane as the medium for chlorosulphonation were found in the literature.

The option of indirect cooling of the vessel contents has been explored and is the main topic of discussion in this paper.Indirect cooling can be done by two ways. By using a jacketed vessel having a spiral baffled jacket or by using heat exchanger where the contents can be made to pass through a heat exchanger like graphite block type heat exchanger. The desired temperature of 5 deg C has to be maintained and would require no dumping of ice clocks into the vessel. Only the amount of water required to decompose excess of chlorosulphonic acid and to make the contents less viscous needs to be added.

This paper presents the details of experiment carried out for external cooling of the sulpho mass and the resulting yield of ASC. The increase in the acidity of the spent acid and the reduction in water consumption is also shown.

II. MANUFACTURING PROCESS

Step 1 Chlorosulphonation of acetanilide

Acetanilide is added gradually to an excess of chlorosulphonic acid in a M. S. jacketed reactor. The batch is then slowly heated to 50°C and maintained at 50°C for 4 hours. The completion of the reaction is checked by caustic solubility test. The liberated hydrochloric acid gas is scrubbed by water in HCI scrubber.

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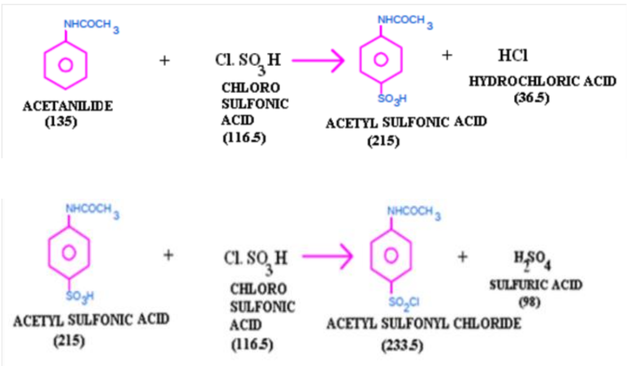
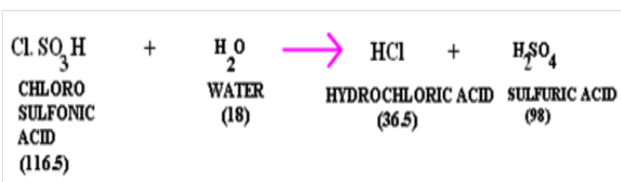


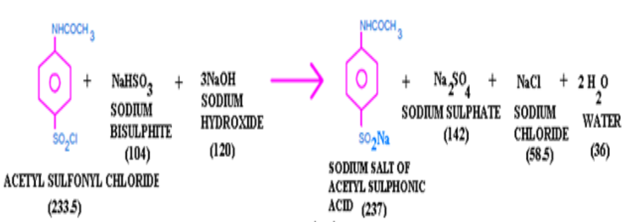
Step 2 Drowning and filtration

The chlorosulphonated mass is added slowly to a well-stirred mixture of ice and water contained in a rubber lined tile lined M.S. tank. The temperature is maintained at 15°-20°C by controlling the addition rate. The slurry is then further stirred for 2 hours at 15°-20°C, to get a filterable product. The isolated sulphonyl chloride is filtered off through a nutsche filter and the wet cake is washed with cold water. The filtrate and the washings are highly acidic liquid effluents consisting of sulphuric acid, hydrochloric acid, and organics in the form of aromatic acids mainly acetanilide sulphonic acid and sulphanilic acid.



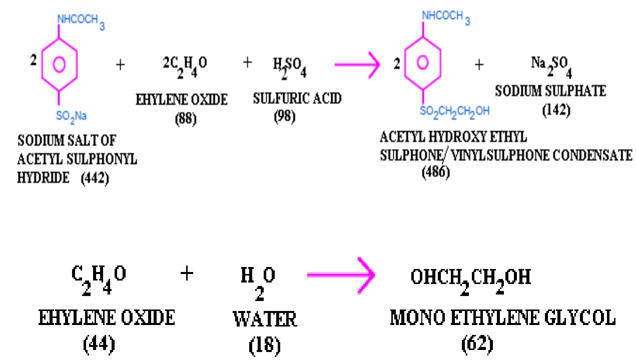
Step 3 Reduction of acetanilide-4-sulphonylchloride

The sulphonyl chloride wet cake is slowly added to an aqueous solution of sodium bisulphite in a S.S. jacketed reduction tank. Caustic lye (48%) is added simultaneously to maintain the pH at 7.5. The mass is stirred till pH stabilises at 7.5 and then it is heated to 50°C and maintained at that temperature.



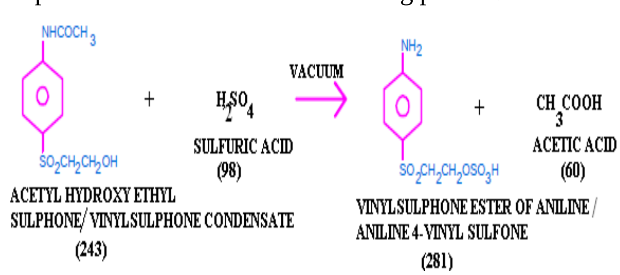
Step 4 Condensation with ethylene oxide

The reaction mass containing the sulphinic acid sodium salt is heated to 50°C in a S.S. Jacketed vessel housed on a flameproof mount. Ethylene oxide gas is then passed at a controlled rate, in 5 hours. All necessary precautions for handling ethylene oxide need to be strictly followed. The pH of the batch is maintained at about 7.5, by addition of the required amount of sulphuric acid. The completion of the reaction is indicated by pH stabilisation at 7.5. The mass is then cooled to 20°C and the precipitated product is filtered through a nutsche filter. The wet cake is washed with water. A large amount of liquid effluent containing organics and inorganic salts is generated at this stage. The wet cake is further dried in a dryer at 100°C, prior to its sulphation hydrolysis.



Step 5 Sulphation cum hydrolysis

Finely powdered acetanilide hydroxy ethyl sulphone is slurried into concentrated sulphuric acid in a S.S. jacketed reactor. The batch is then slowly heated to 125°C and stirred for 5 hours. The reaction is complete when the evolution of acetic acid and water ceases and the temperature of the reaction mixture starts falling. End point of the reaction is also confirmed by TLC. Acetic acid generated at this stage is recovered by condensation along with water. The product is obtained as a powder which is then taken to pulveriser and blender before being packed.



III. PROCESS CONSIDERATIONS

The following are the main points to be considered in the chlorosulphonation and dumping steps of the process.

1) ASC gets hydrolysed back to ASA at higher temperature.
2) Precipitation of sulphanilic acid favoured by lower amount of water and lower temperature.
3) Better recovery of HCl at higher concentration of spent acid even at lower temperature.
4) Higher strength and purity of spent acid with lower amount of water.

All the points mentioned above can be simultaneously satisfied by using external cooling. This can provide optimum yields of ASC, with maximum recovery of HCI, SA and spent acid of acceptable quality and concentration
along with the obvious reduction of effluent load and ice consumption.

IV. EXTERNAL COOLING EXPERIMENT

Figure 1: Experimental setup

The apparatus setup is shown in the above figure. The procedure undertaken is as follows

- A round bottom flask with thermopocket was taken and 200 ml of water added in it.
- Then 150 ml of sulpho mass coming from the chlorosulphonation step was added gradually with constant stirring.
- The RBF was placed in a bucket filled with dry ice to maintain the temperature around 5 deg C.
- The decomposition of CSA was allowed for 1 hr when the contents of the flask turned white and viscous.
- The wet paste of ASC was filtered under vacuum and given 3 washes with water to produce a cake having moisture of about 10 %.

Results:

Sulpho mass taken = 150 ml = 216 gms

Water taken = 200 ml = 200 gm

Temp. maintained = 5 deg C

Acetyl Sulphonyl Chloride ASC obtained = 150 gm (10% H2O) = 135 gm pure ASC.

Acidity of spent acid obtained = 55 %

Reaction time = 1 hr

Comparison of experimental results with plant data

1) Yield of ASC:

Process	**Sulpho mass**	**ASC obtained**	**Yield (w/w of sulpho mass)**
Plant	15.7 tonnes	3.9 tonnes	24.8 %
Experiment	216 gm	135 gm	62.5 %

2) Water/ice consumption

Water is needed for decomposing the excess of chlorosulphonic acid CSA coming from the chlorosulphonation step. This produces HCl and sulphuric acid. But additional water is also needed for making the contents flow. In the experiment, initially trials were taken to find the minimum quantity of water needed.

Trials	**Water taken, ml**	**Nature of contents**
1	100	Very viscous, stirring stopped

2	150	Very viscous, rpm had to be kept maximum
3	200	Less viscous under normal rpm of stirrer

Process	**Water/ice added**	**Sulpho mass**	**water quantity**
Plant	30 tonnes	15.7 tonnes	1.91 times sulpho mass
Experiment	200 gm	216 gm	0.925 times sulpho mass

3) *Spent acid*

Process	**Spent acid strength**
Plant	15 %
Experiment	55 %

Figure 2: ASC cake from vaccuum filtration

Following can be inferred from the above experiment:

- External cooling results in decreasing the water content in the product by more than 50 %. This means 50% reduction in the effluent load.
- The yield of ASC in the experiment is found to be 2.46 times of that obtained in the plant.
- Spent acid produced from the experiment is of strength 55% compared to 15% produced in the plant.
  The increased concentration of spent acid means that the recovery of HCl from it will also be easier. And the spent acid itself can also find some use in some other organic industry.

V. CONCLUSION

In today's modern world of ours, there is an ever increasing attention and efforts towards minimizing the wastes as much as possible. The conventional methods which are being practiced in many chemical industries are to be replaced with new approaches which are economically beneficial as well as environmental friendly.

The experimental results obtained above conclude that maintaining low temperature through external cooling of the vessel can provide a number of advantages in the vinyl sulphone industry which is one of the most important dye intermediate industry in the country. Increase in yield of ASC, concentrated spent acid and reduction in effluent has been noted in the experiment. Moreover, this will lead to better recovery of byproducts like HCl and sulphanillic acid. Ice addition can be completely eliminated and external cooling can be provided either by jacketed vessel having a spiral baffled jacket or by using a graphite block type heat exchanger. Chilled brine can be used in both the cases.

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